

PATENT SPECIFICATION

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(54) CONTINUOUS PROCESS FOR PRODUCING TEREPHTHALIC ACID

(71) We, MITSUBISHI CHEMICAL INDUSTRIES LIMITED, a Japanese body corporate of 5-2, Marunouchi 2-Chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 This invention relates to a process for producing acid by the oxidation of *p*-xylene. 5
 In a known process, the so-called "SD process", *p*-xylene in acetic acid as solvent is oxidized with molecular oxygen in the presence of a heavy metal oxidation catalyst system. The terephthalic acid produced is isolated from the slurry produced by centrifugal separation and the mother liquor separated is usually distilled to separate water and a residue containing 10 the catalyst and to recover acetic acid for reuse. Because the mother liquor contains valuable materials, for example unreacted *p*-xylene, catalyst and oxidation intermediates, it is desirable from a commercial point of view to recycle the mother liquor to the oxidation step. However, the mother liquor also contains small amounts of other materials which adversely affect the reaction, and, therefore, if the mother liquor is recycled, undesirable side reactions 15 will occur to impair the quality of the terephthalic acid product. Thus, in practice, recycling the mother liquor has hitherto been impossible without causing disadvantages as mentioned above.

It has now been found, in accordance with the present invention, that if the slurry obtained in the oxidation reaction is directly subjected to a post-oxidation treatment without separation 20 of the terephthalic acid, the mother liquor can be recycled to the oxidation reactor without having adverse effects on the oxidation reaction and highly quality terephthalic acid may thus be obtained.

Accordingly, the invention provides a continuous process for producing terephthalic acid by oxidising *p*-xylene with molecular oxygen in acetic acid as solvent in the presence of an 25 oxidation catalyst comprising a cobalt compound, a manganese compound and hydrogen bromide, at a temperature from 150°C to 250°C under a pressure of from atmospheric to 200 atmospheres; in which

- (a) the water-content of the reaction mixture in the oxidation step is controlled by discarding water condensed from the gases discharged from the oxidation step and 30 introducing acetic acid to the oxidation step;
- (b) post-oxidation of the terephthalic acid slurry from the oxidation step is effected, without the addition of *p*-xylene, at a temperature of from the oxidation temperature to 50°C below the oxidation temperature; and
- (c) at least a portion of the mother liquor separated from the slurry obtained in step (b) is 35 recycled to the oxidation step.

The present invention may be applied to any process in which *p*-xylene in acetic acid is oxidised in the liquid phase with molecular oxygen in the presence of a catalyst comprising a cobalt compound, a manganese compound and hydrogen bromide, at a temperature of from 150°C to 250°C under a pressure of from atmosphere to 200° atmospheres. A typical 40 example of such a process is the so-called SD process the details of which are disclosed in United States Patent No. 2,833,816.

The solvent is usually used in an amount of from 0.5 to 20, preferably from 1 to 10, parts by weight per part by weight of the *p*-xylene. The solvent may contain water or a reaction promoter, such as an aldehyde, a ketone, an alcohol or paraldehyde.

45 The catalyst employed in this invention is a known Co-Mn-Br ternary catalyst system. 45

Cobalt and manganese compounds suitable for use in the catalyst system are disclosed in United States Patent No. 2,833,816; and thus, for example, the catalyst system may contain as cobalt compound, cobalt acetate, cobalt bromide or cobalt naphthenate and, as manganese compound, manganese acetate, manganese bromide or manganese naphthenate. It is essential that all or a part of the bromine compound be hydrogen bromide. When cobalt bromide and/or manganese bromide are used, the amount of hydrogen bromide in the catalyst system can be reduced since such compounds contain bromine.

In the prior art oxidation of *p*-xylene with molecular oxygen, sodium bromide has been used as a typical bromine source in the catalyst. Due to the loss of a part of the bromine during the reaction the addition of further bromine compound is required in order to maintain the predetermined bromine concentration in the reaction system. However, the addition of sodium bromide increases the concentration of sodium ions in the mother liquor which is recycled, since an amount of sodium ions corresponding to that of the lost bromine remains. Such excess sodium ions adversely affect the oxidation reaction. Therefore, according to this invention, the use of hydrogen bromide as the bromine source is significant with respect to recycling the mother liquor to the oxidation step without adversely affecting the reaction. The catalyst components are suitably present in amounts sufficient to provide from 200 to 5000 ppm, preferably from 200 to 600 ppm, of Co, from 10 to 1000 ppm, preferably from 100 to 600 ppm, and Mn and from 400 to 10,000 ppm, preferably from 600 to 2000 ppm, of Br, based on the solvent. When the amount of catalyst used is within the above range, the oxidation reaction is successfully carried out while the mother liquor is recycled.

The temperature at which the oxidation is carried out is from 150 to 250°C and, where the amount of catalyst used is within the above range, the temperature is preferably from 170 to 230°C, more preferably from 205 to 225°C. The pressure under which the oxidation is carried out is from atmospheric to 200 atm., preferably from atmospheric to 100 atm.

The gas containing molecular oxygen supplied to the liquid phase containing the *p*-xylene is usually air and the amount thereof supplied is from 1 to 100 moles, preferably 3 to 100 moles of oxygen, per mole of the material to be oxidized.

In the oxidation reactor, at least 95% by weight of *p*-xylene is oxidized, preferably more than 98%, especially more than 99%.

The reaction product slurry obtained from the oxidation reaction is then subjected to post-oxidation treatment without isolating the terephthalic acid. The purpose of this treatment is to further oxidize the oxidation intermediates present in the slurry and the oxygen content of the molecular oxygen-containing gas supplied to this treatment may be lower than that supplied to the oxidation reaction. Conveniently, a portion of the exhaust gas from the oxidation reactor is used. The post-oxidation is carried out at a temperature of from the oxidation temperature to a temperature of 50°C, preferably 30°C, below that of the oxidation reaction. In the post-oxidation, no further catalyst may be required. The post-oxidation may be effected in a separate post-oxidation vessel or in a cooling crystallizer in which the post-oxidation and crystallization are concurrently carried out while cooling. Process wherein xylene is oxidized to terephthalic acid by a first oxidation followed by a post-oxidation at a temperature equal to or below the oxidation temperature, are described and claimed in our copending application Nos. 1,454,478 and 3888/77. (Serial No. 1577019).

The slurry which has been subjected to the post-oxidation is then cooled to effect crystallization, in the usual manner, and separated into terephthalic acid and mother liquor by the centrifugal separator. It is essential according to this invention that at least a part of the mother liquor be recycled as it is to the oxidation reactor. The amount of mother liquor to be recycled is suitably from 20 to 80%, preferably from 50 to 80%, by weight.

It is preferred that the remaining, unrecycled mother liquor be introduced into a distillation column in which water is removed and acetic acid is recovered. The recovered acetic acid may be reused in the oxidation step, if desired.

From the distillation residue, metallic catalyst components may be recovered by extracting the residue with water, followed by adding a carbonate compound to precipitate carbonates of metallic components, washing the precipitate with water and dissolving it in acetic acid. The acetates thus recovered can be introduced into the oxidation step.

In order to recycle the mother liquor as it is to the oxidation reactor, it is necessary to remove water which is formed during the reaction. Because too high a water concentration adversely affects the reaction, it is preferred that, in general, the water concentration of the mother liquor in the oxidation reaction mixture be maintained at less than 20% by weight.

The water concentration is controlled by removing water from the oxidation system and this is achieved by condensing at least a portion of the condensable gases from the oxidation reaction to produce a water-containing condensate and discarding water therefrom. In commercial operations it is generally desirable to recover solvent (i.e. acetic acid) from the condensate and this may be achieved by distilling the condensate in a distillation column so as to separate out water and recover the solvent for reuse.

It is not always necessary to install such a distillation column separately from the reactor, and the distillation column used may be of a type such that the column is directly connected to the top of the reactor so that water and non-condensable gas are removed from the top of the column and condensable gas is returned to the reactor. In general, the condensable gas discharged from the reactor is condensed in the condenser, and most of the condensate is returned to the reactor and only a portion thereof is introduced into the distillation column.

The distillation is usually carried out under atmospheric pressure and at a bottom temperature of about 124°C and at a top temperature of about 100°C. The solvent recovered is recycled to the oxidation reactor.

The continuous process according to this invention will now be described with reference to the accompanying drawing which is a block diagram illustrating one embodiment for the production of terephthalic acid.

In the apparatus shown in the drawing *p*-xylene is fed via pipeline 10 to an oxidation reactor I which is also supplied with catalyst and acetic acid via pipeline 12 and air via pipeline 14 to effect the oxidation reaction.

The slurry produced in reaction I is transferred via pipeline 16 into post-oxidation reactor II into which air diluted with an inert diluent is blown via pipeline 18 to effect the post-oxidation treatment. The post-oxidation slurry is transferred from reactor II via pipeline 20 to crystallizer III in which crystallization is effected to thoroughly precipitate terephthalic acid, which is then separated from the slurry in centrifugal separator IV and thence recovered via pipeline 22. The mother liquor from the slurry is recycled via pipelines 24 and 26 to oxidation vessel I, while a portion thereof is removed via pipeline 28.

The condensable gas which is formed during the oxidation reaction and discharged via pipeline 30 from the top of oxidation reactor I is condensed in condenser 32 and the most of the condensate is returned to the oxidation reactor, the remainder being introduced via pipeline 34 to distillation column V, from the top of which water is removed via pipeline 36 and from the bottom of which the solvent is recovered and recycled via pipeline 26 to oxidation reactor I.

As mentioned above, the solvent and the mother liquor which have been recovered are recycled to oxidation reactor I via pipelines 24 and 26, while fresh catalyst and solvent are added via pipeline 12 to make up for what has been lost and removed whereby the operation is carried out continuously.

According to this invention, if the mother liquor of the slurry is recycled as it is to the oxidation reactor, the reaction is not adversely affected and high quality terephthalic acid can be obtained. Further, various valuable components in the mother liquor, such as *p*-xylene oxidation intermediates and catalysts, are completely utilized to make this process commercially attractive. The reason why the reaction is not impaired when the mother liquor is recycled is that, with the post-oxidation of the oxidation product slurry, the materials which would otherwise impair the reaction are substantially removed.

In order that the invention may be well understood the following Examples are given by way of illustration only.

The Examples were carried out in apparatus as shown schematically in the accompanying drawing except that, as noted more fully below, distillation Column V was omitted.

Example 1

Into a 10 litre capacity titanium autoclave reactor I equipped with a stirrer and an external heater was charged a mixture of 3 litres of acetic acid (water content: 5% by weight), 4.43 g of cobalt acetate tetrahydrate, 4.68 g of manganese acetate tetrahydrate and 6.79 g of hydrobromic acid (47% aqueous solution), and then *p*-xylene was supplied via pipeline 10 at a rate of 750 g/hr and air was supplied via pipeline 14 at such a rate that the oxygen concentration of the exhaust gas from the reactor was 4 to 5% by volume, while the reaction conditions, reaction temperature of 210°C and reaction pressure 24 kg/cm², were maintained for 1.5 hours to effect semicontinuous reaction. Then, a freshly prepared mixture of acetic acid and catalyst having the above composition was supplied via pipeline 12 at a rate of 2,250 g/hr, while the slurry was discharged via pipeline 16 at a rate of 3,600 g/hr to effect a continuous oxidation reaction with an average residence time of 60 minutes. The slurry discharged from reactor I was supplied to a 10 litre capacity titanium autoclave II (the post-oxidation vessel) equipped with a stirrer and an external heater to which diluted air having an oxygen concentration of 14% by volume was supplied via pipeline 18 at such a rate that the oxygen concentration of the exhaust gas from the post-oxidation vessel was maintained at 3 to 4% by volume, with the reaction conditions of a temperature of 195°C, a pressure of 19 kg/cm² and an average residence time of 40 minutes. The post-oxidized slurry was transferred to crystallizer III in which crystallization was effected at 100°C and terephthalic acid and the reaction mother liquor were then separated in centrifugal separator IV.

After 3 hours from the start of the continuous oxidation reaction, a portion of the mother liquor to which fresh hydrogen bromide had been added in an amount corresponding to that

lost during the reaction was recycled to the reactor I via pipelines 24 to 26 at a rate of 1250 g/hr (the recycling being 50%) and the remainder of the mother liquor was removed via pipeline 28. The amount of acetic acid solvent containing the catalyst supplied via pipe 12 was decreased to 1100 g/hr. In order to prevent an increase in the water content of the mother liquor in the reactor I due to the recycling of the mother liquor, a portion of the condensable gas accompanying the exhaust gas from the reactor was withdrawn after 3 hours from the start of the continuous reaction via pipeline 34, and acetic acid was supplied through pipe 26 in such an amount as contained in the condensate withdrawn to maintain the water concentration of the mother liquor in the reactor at 18% by weight (in commercial operation the said acetic acid would be recovered from the distillation column, but in this Example the column was not used).

After continuing such mother liquor recycling for 30 hours, the terephthalic acid obtained by solid-liquid separation was suspended in three times its weight of acetic acid and agitation was continued at a temperature of 80°C to 20 minutes to effect washing. The properties of the terephthalic acid thus obtained are given in Table 1.

Comparative Example 1

The procedure of Example 1 was repeated to carry out continuous oxidation except that the steps of recycling the mother liquor and withdrawing a portion of the condensate were omitted. The properties of the terephthalic acid thus obtained are given in Table 1.

As is clear from Example 1 and Comparative Example 1, the properties of terephthalic acid obtained by effecting post-oxidation and recycling the mother liquor to the oxidation reactor are comparable with those of the terephthalic acid obtained in Comparative Example 1 which does not involve recycling the mother liquor and which gives good results.

Example 2

The procedure of Example 1 was repeated except that the amount of acetic acid containing the catalyst supplied via pipeline 12 was 680 g/hr and the amount of mother liquor recycled via pipelines 24 to 26 was 1730 g/hr (70% of the mother liquor separated being recycled). The properties of the terephthalic acid obtained are given in Table 1.

From the results, it is clear that in Example 2 the amount of mother liquor to be recycled can be increased to 70% by weight without adversely affecting the properties of the terephthalic acid as compared with those obtained in Example 1 (recycling being 50%) and Comparative Example 1 (no recycling).

Comparative Example 2

The procedure of Comparative Example 1 was repeated to carry out continuous oxidation reaction for 30 hours except that *p*-xylene was supplied at 500 g/hr, the semicontinuous reaction time was 2 hours, acetic acid containing the catalyst was supplied in the continuous reaction at a rate of 1500 g/hr and the average residence time in reactor I was 90 minutes; and no post-oxidation was carried out. The properties of the terephthalic acid obtained are given in Table 1.

Comparative Example 3

The procedure of Comparative Example 2 was repeated except that, after 4 hours from the start of the continuous reaction, the reaction mother liquor was recycled through pipelines 24 and 26 at a rate of 830 g/hr and the amount of acetic acid solvent containing the catalyst supplied through pipeline 12 was decreased to 750 g/hr, while the water concentration of the mother liquor in reactor I was maintained at 18% in the same manner as in Example 1 and recycling of the mother liquor was continued for 30 hours. The properties of the terephthalic acid thus obtained are given in Table 1.

As is clear from the results, the terephthalic acid produced by recycling to the reactor a mother liquor which has not been subjected to post-oxidation (Comparative Example 3) contains much more 4-carboxy-benzaldehyde as an oxidation intermediate impurity and its transmittance is lower in comparison with the terephthalic acid produced without recycling the mother liquor and effecting post-oxidation (Comparative Example 2).

Example 3

The procedure of Example 1 was repeated except that *p*-xylene was supplied at a rate of 500 g/hr, the semicontinuous reaction time was 2 hours, acetic acid containing the catalyst was supplied in the continuous reaction at a rate of 1500 g/hr, the average residence time in the reactor I was 90 minutes, and, after 3 hours from the start of continuous reaction, the mother liquor was recycled at 830 g/hr and the acetic acid containing the catalyst was supplied at 750 g/hr. The properties of the terephthalic acid thus obtained are given in Table 1.

Comparative Example 4

The procedure of Example 3 was repeated except that the steps of recycling the mother liquor and withdrawing a portion of the condensate were omitted. The properties of the resulting terephthalic acid are given in Table 1.

TABLE I

| | | Ex. 1 | Ex. 2 | Comp. Ex. 1 | Comp. Ex. 2 | Comp. Ex. 3 | Ex. 3 | Comp. Ex. 4 | |
|----|--|-------|-------|----------------|----------------|----------------|-------|----------------|----|
| 5 | 4-CBA * concentration in the product terephthalic acid (ppm) | 460 | 460 | 450 | 400 | 580 | 280 | 270 | 5 |
| 10 | Transmittance (%) | | | | | | | | 10 |
| | 340 mμ | 88 | 87.5 | 89 | 84 | 77 | 91.0 | 91.5 | |
| | 400 mμ | 98.5 | 98.0 | 98.5 | 98.5 | 97.5 | 99.0 | 99.0 | |
| 15 | Residence time (min). | 60 | 60 | 60 | 90 | 90 | 90 | 90 | 15 |
| 20 | Post-oxidation | done | done | done | none | none | done | done | 20 |
| | Recycling mother liquor | done | done | none | none | done | done | none | |
| 25 | Amount of mother liquor recycled (% by weight) | 50 | 70 | - | - | 50 | 50 | - | 25 |

30 * Note 4-CBA: 4-Carboxybenzaldehyde

WHAT WE CLAIM IS:-

1. A continuous process for producing terephthalic acid by oxidizing *p*-xylene with molecular oxygen in acetic acid as solvent in the presence of an oxidation catalyst comprising a cobalt compound, a manganese compound and hydrogen bromide, at a temperature of from 150°C to 250°C under a pressure of from atmospheric to 200 atmospheres; in which
 - (a) the water-content of the reaction mixture in the oxidation step is controlled by discarding water condensed from the gas discharged from the oxidation step and introducing acetic acid to the oxidation step;
 - (b) post-oxidation of the terephthalic acid slurry from the oxidation step is effected, without the addition of *p*-xylene, at a temperature of from the oxidation temperature to 50°C below the oxidation temperature; and
 - (c) at least a portion of the mother liquor separated from the slurry obtained in step (b) is recycled to the oxidation step.
2. A process as claimed in claim 1 in which step (a) is effected by introducing at least a portion of the condensable gas discharged from the oxidation step to a distillation column to remove water and recover solvent and recycling recovered solvent to the oxidation step.
3. A process as claimed in claim 1 or claim 2 in which from 20 to 80% by weight of the mother liquor is recycled to the oxidation step.
4. A process as claimed in any one of the preceding claims in which the water content of the mother liquor in the oxidation step is maintained at less than 20% by weight.
5. A process as claimed in any one of the preceding claims in which the mother liquor and terephthalic acid are separated from the slurry obtained in step (b) by centrifugal separation.
6. A process as claimed in any one of the preceding claims in which the cobalt compound is cobalt acetate and the manganese compound is manganese acetate.
7. A process as claimed in claim 1 substantially as hereinbefore described with reference to the accompanying drawing.
8. A process as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.
9. Terephthalic acid when obtained by a process as claimed in any one of the preceding claims.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

